JAPANESE [JP,07-278510,A]

CLAIMS DETAILED DESCRIPTION TECHNICAL FIELD PRIOR ART EFFECT OF THE INVENTION TECHNICAL PROBLEM MEANS EXAMPLE

[Translation done.]

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DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Industrial Application]This invention relates to the hot melt adhesive having the resolvability by a microorganism.
[0002]
[Description of the Prior Art]Hot melt adhesive is solid adhesives at the ordinary temperature of the 100% solid content which used thermoplastics as the main ingredients. Heat melting can be carried out in the spreading machine called an applicator, it can apply to adherend by a molten state, and adhesion can be completed in several seconds after sticking by pressure. Although there are sulfur, asphalt, a wax to carry out heat melting, apply, make it solidify by cold energy, and obtain adhesive strength, etc. for many years, Hot melt adhesive here is the multicomponent system adhesives with which the workability at the time of adhesion and the performance after adhesion used as the main ingredients the thermoplastics fully taken into consideration. Since hot melt adhesive contains neither water nor a solvent and it needs neither drying time nor a dryer, adhesion can complete adhesives by

sticking by pressure of an after-application short time. Since there is such an advantage, hot melt adhesive is widely used for all the industrial fields nowadays as a thing suitable for improvement in the speed of adhesion, and pollution-free-ization at the time of adhesion.

[0003]As an ingredient which constitutes hot melt adhesive, it is thermoplastics, a tackifier, and waxes and an antioxidant and a bulking agent are blended if needed. Workability (melt viscosity, an open time, a solidification speed, thermal stability, etc.) and performances (adhesiveness, heat resistance, cold resistance, etc.) are taken into consideration, and the rate of each ingredient is determined. The combination ingredient and role of hot melt adhesive are explained below.

[0004]Thermoplastics (base polymer)

It is that excel in cohesive force, adhesive strength, and flexibility, and also compatibility with other resin is good as base polymer conditions. Although it is ethylene-acetic acid vinyl polymer (EVA), polyethylene, atactic polypropylene (APP), an ethylene ethyl acrylate copolymer (EEA), polyamide, polyester, etc. are one of those are used most widely now.

[0005]Tackifier (tacky fire)

The conditions which should possess a tackifier lower melt viscosity and improve the workability at the time of spreading at the same time it dissolves with base polymer and they give hot tuck nature to adhesives. Although the resin which used natural articles, such as a rosin derivative and a terpene, conventionally had mainly been used as such a tackifier, the quality of hydrocarbon resin, such as petroleum resin, reaches for improving, and it came to overwhelm a natural product.

[0006]A wax wax is used for physical-properties adjustment of lowering the melt viscosity of adhesives, an open time, softening temperature, hardness, hot tuck nature, blocking nature, etc. Although it is very convenient, depending on an addition, contraction of the extreme fall of adhesive strength and adhesives also becomes large.

[0007]When used for a paper label, a biodegradable plastic, etc., in order not to decompose, the hot melt adhesive made from such a raw material remained all over the reclaimed ground or the river lake as a lump, and the problem had produced it.

[0008]

[Problem(s) to be Solved by the Invention]The conventional hot melt adhesive is excellent in points, such as economical efficiency and safety, and is used for a package, bookbinding, a plywood, woodwork relations, etc. which are the mass consumption fields. It is thought that adhesives suitable for an environmental problem etc. are required from now on. For example, as for containers, such as a

shampoo, there was a problem in processing of a used thing. That is, with the container made from a plastic, since it was chemical very stable, it burned with the special incinerator, or the method only had reclaiming land as it is. It cannot be said on the problem of environmental pollution, etc. that it is desirable so that concern may increase especially about reclamation in recent years. Then, the biodegradable plastic attracts attention globally these days as one of the solution of the global environment problems by a waste plastic. This biodegradable plastic came to be used for a plastic container etc. However, there was no biodegradable adhesive used for this biodegradable plastic container until now.

[0009]

[Means for Solving the Problem]In order to solve such a problem, this invention is originated and the purpose is to provide hot melt adhesive provided with microbial degradability.

[0010]This invention relates to biodegradable hot melt adhesive which consists of raw rosin 100 weight section, ten to crude rubber 200 weight section, a vegetable system, or ten to mineral system wax 200 weight section.

[0011]A milky lotion (latex) produced by crude rubber used for this invention damaging a bark of Hevea braziliensis (Hevea brasiliensis) is collected, It is manufactured by performing filtration, coagulation, rolling, smoking, a drainer, hot air drying, etc., and the main ingredients are ****- 1,4-polyisoprene. With a manufacturing method, although there are a smoked sheet, pale crepe, and a HEBEA crumb, all can be used as biodegradable hot melt adhesive of this invention. With natural rubber latex used for this invention, what collected a milky lotion (latex) produced by damaging a bark of Hevea braziliensis is made stability with ammonia. If fresh latex is observed under a microscope, a size different rubber particle from which shape differs is carrying out Brownian motion actively. Since it is wrapped in a proteinic protective film, the surface is charged in negative and a rubber particle is repelled mutually, thereby, a colloidal system of latex is maintaining stability. A size of this latex particle is 0.1-0.5 micron in diameter.

[0012]The surface of a rubber particle in latex is wrapped in a layer of phospholipid and protein, and is protected. This protective layer is carrying out an important role which opts for the stability of latex, and a colloid action. Although combination with a rubber particle, and phospholipid and protein is quite firm, it is a well-known fact that it is ****- 1,4-polyisoprene already, and a number average molecular weight is 100,000 to about 1 million. Since latex extracted from a tree has many uneconomical moisture for conveying to a consumer place by 30 to 40% of a rubber part, it has condensed a part for rubber to 60 to 70%. There are a centrifuge

method, the creaming method, an evaporation method, an electric gradient method, etc. in a condensation method. Although fresh latex is pH 7 neutrally generally, if it is neglected, acidity will be spontaneously coagulated in increase and the pH 5 neighborhood in an operation of bacteria and an enzyme. In order to prevent this, after usual natural rubber latex condenses, it adds ammonia and is maintaining pH 9-10, i.e., alkalinity. Also in the stable state where ammonia was added, although phospholipid and protein are disassembled gradually, since higher-fatty-acid soap is generated and protected by rubber particle protective layer, it is changeless at stability. Biodegradability falls [crude rubber which carried out crosslinking treatment, such as vulcanization,].

[0013]Raw rosin used for this invention is extracted from a Pinus group variety of Pinaceae, is the method of extraction and can be classified to about three. Most, it is gum rosin, and eyes cover turpentine which cut and extracted a bark into V character over steam distillation, they remove ****** and remain. The second is wood rosin and is obtained by solvent extraction of a stump of a pine. The third collects sludge which comes out from a paper mill, and it is tall oil rosin and it is obtained by fractionating. Raw rosin consists of not less than 90% of resin acid, and about 10% of neutral substances, and the main ingredients of resin acid are abietic acid, REBOPIMARU acid, neoabietic acid, parous thorin acid, etc. That it can be used as raw rosin of this invention has gum rosin, wood rosin, tall oil rosin, etc.

[0014]A wax used for this invention is a vegetable system wax or mineral system petroleum wax, and are a caster wax, the KARUBANA wax No. 2, Camps Delia, soybean hydrogenated oil, a rice wax, 180 ** micro wax, paraffin wax, and a montan wax especially. Fats and oils which a wax says ester with insolubility high-class monohydric alcohol or dihydric alcohol to fatty acid and water, and use ester of fatty acid and glycerin as the main ingredients are a thing of another kind. A vegetable system wax is shown in vegetable epidermis, and prevents the humidity, desiccation, etc., and has an operation of heat insulation. Although a kind of wax of mineral system petroleum wax is various, generally there are paraffin wax, microcrystallin wax, etc. A mixture of a straight chain hydrocarbon called n-paraffin from the carbon number 25 to about 35 is a subject, and paraffin wax differs in character greatly with the mixing ratio, including isoparaffin and cycloparaffin in large quantities. Since the presentation of paraffin is comparatively simple, character does not have diversity, either, but micro wax can give the feature to pliability, an adhesive property, thermal stability, cold resistance, etc.

[0015]Decomposing bacteria of such crude rubber are bacilli which inhabit common soil, and are not special bacilli. It is known that

decomposing bacteria of crude rubber are a Nocardia [Doi and others (JP,63-5426,B, a Japanese agricultural academic journal, 65,981 (1991), Appl.Environ. Microbiol.50,965 (1985))] group, or a Rhodococcus group. The biodegradability of a wax used for this invention is a bacillus which lives into common soil, and is not a special bacillus. The biodegradability of waxes is reported by paper (oil recovery study, 36 and 46 (1987), oil recovery study, 36,852 (1987)) of former some.

[0016]In this invention, as a bulking agent, a softener, and an antioxidant, calcium carbonate, Clay, a zinc oxide, a titanium dioxide, process oil, extender oil, It does not interfere, even if it adds polyisobutylene, polybutene, liquefied polyisoprene, and 2,6-di-butyl-4-methyl phenol, styrene-ized phenol, 2,5-di-tert-butylhydroquinone, etc. This invention is applied to hot melt adhesive which needs biodegradability.

[0017]a presentation of raw rosin, crude rubber, and a wax receives raw rosin 100 weight section -- crude rubber -- ten to 200 weight section, it is preferably used at a rate of 20 to 150 weight section, and a wax is 20 to 100 weight section preferably ten to 200 weight section to raw rosin 100 weight section. Holding power declines that they are ten or less weight sections, to raw rosin 100 weight section, even if it applies heat as they are 200 or more weight sections, it does not dissolve, and crude rubber does not become hot melt adhesive. A wax becomes it hard that they are ten or less weight sections to raw rosin, and adhesive strength declines that speed is slow and is 200 or more weight sections.

[0018]

[Example]Below, an example explains the adhesives of this invention. A weight section is expressed as a part among an example, and weight % is expressed as %, respectively.

Biodegradable sample student rosin of example 1 rosin (China rosin)

The bacillus contained in the soil which extracted the ground was extracted and used for the microbial suspension from rosin ester hydrogenation rosin ester dibasic acid denaturation rosin ester polymerization rosin ester soil from Hokkaido, Akita Prefecture, Miyagi Prefecture, Ibaragi Prefecture, Chiba Prefecture, Tokyo, Gumma Prefecture, Shizuoka Prefecture, Ehime Prefecture, and Okayama Prefecture. As the training culture medium, the synthetic medium which consists of mineral as shown in Table 1 was used. 30 mg of powder and 0.06 ml of microbial suspension of raw rosin are added and cultivated to 40 ml of this culture medium. Culture was performed 80th [about] day from 14 at 30 **, and shake was performed by 250 round trip/, aerating.

[0019]

[Table 1]

$(NH_4)_2SO_4$	2.0g
KH_2PO_4	1.5g
$NaHPO_4 \cdot 12H_2O$	1.5g
$MgSO_4 \cdot 7H_2O$	0.5g
NaCl	0.1g
$CaCl \cdot 2H_2O$	0.02g
$FeSO_4 \cdot 7H_2O$	0.01g
$MnSO_4 \cdot 4 \sim 6H_2O$	2.0mg
$ZnSO_4 \cdot 7H_2O$	2.0mg
$Na_2MoO_4 \cdot 2H_2O$	2.0mg
超純水	1l
NaOHでpHを7.2に調製	

[0020]Only the bacillus performed (the comparative example 2) and the rosin derivative (rosin ester, hydrogenation rosin ester, dibasic acid denaturation rosin ester, polymerization rosin ester) + bacillus (comparative examples 3-6) in the similar way without putting in a bacillus and only raw rosin's putting in (the comparative example 1) and rosin as one to comparative example 6 comparative example.
0.45-micrometer filtration is performed for the culture medium cultivated between about 80 days of measurement of organic carbon (TOC) in parameter 1 culture medium, About what performed dilution one to 100,000 times, the culture medium cultivated between about 80 days of measurement of 2 number of microorganism which diluted suitably [after removing floating matter] and measured TOC. It cultivated by the culture medium (it abbreviates to NB agar plate culture medium below) which mixed agar to (Nutrient Broth by DIFCO), and the number of micro organisms per ml was measured.
The value of result 1TOC shows the carbon content of the ingredient of the rosin which began to melt into solution. The value of TOC of Example 1 which put in the bacillus is because small one disassembled the rosin which began to melt as compared with the comparative example 1.
2) In Example 1 which put in the bacillus, since rosin was increased as a nutrient, it turns out that the number of bacilli is increasing about 100 times rather than the comparative example 2.
3) Since biodegradability does not have a rosin derivative, no systems of a rosin derivative + bacillus change from the measurement to the comparative example 2 of TOC concentration and number of microorganism. That is, it turns out that there is no growth of a microorganism.
As mentioned above, it turns out that a rosin derivative does not have that raw rosin has biodegradability.
[0021]
[Table 2]

		ＴＯＣ(ppm)	生菌数(CFU)
実施例 1	生ロジン＋菌	330	6.7×10^{7}
比較例 1	生ロジンのみ	1160	0.0
比較例 2	菌のみ	2	9.2×10^{5}
比較例 3	ロジンエステル	3	1.4×10^{5}
比較例 4	水添エステルロジン	5	2.3×10^{5}
比較例 5	二塩基酸変性ロジンエステル	4	2.2×10^{5}
比較例 6	重合ロジンエステル	5	1.5×10^{5}

CFU:colony forming unit (生菌数)

[0022]Example 2 - the biodegradable sample crude rubber pale crepe of 6 crude rubber (ten mastications, 0 times)
Smoked sheet HEBEA crumb natural-rubber-latex (lump which dried crude rubber which carried out moisture powder was used.) culture medium was prepared like the comparative example 1, added the lump of 0.5 g of the above-mentioned crude rubber (it sterilized by ethanol 70%), and was performed.
At the relative humidity of 50**5%, and the temperature of 23**2 **, the gravimetry after the early stages of a parameter 1 gravimetry sample and processing was performed, after controlling the humidity for 48 hours or more. The sample of the above-mentioned crude rubber performed between 40 days of culture was washed in cold water so that it might not damage, and after drying, it performed the gravimetry. Measured value was performed to mg and calculated weight retention by the following formula about each sample.
Weight retention =100x (W2/W1) (%) .... Formula (1)
Here, it is change analytical method:GPC (Gel Permeation Chromatography) of weight 2 molecular weight after the weight W2:culture before W1:culture.
A preparing method of a sample: The dried crude rubber was melted in THF and only the portion of fusibility was measured.
Result[0023]
[Table 3]

		実施例 2 ﾍﾟｰﾙｸﾚｰﾌﾟ 素練りなし	実施例 3 ﾍﾟｰﾙｸﾚｰﾌﾟ 素練り10回	実施例 4 ｽﾓｰｸﾄﾞｼｰﾄ	実施例 5 ﾍﾍﾞｱｸﾗﾑ
重変 量化	培養後／培養前	88%	88%	92%	96%
平分子均量	培養前	18.0×10^5	15.6×10^5	13.8×10^5	14.2×10^5
	培養後	8.5×10^5	6.0×10^5	10.1×10^5	10.7×10^5

[0024]1) As for the weight of the crude rubber of the culture medium into which the microorganism was put, it turned out that weight is decreasing about ten percent only compared with crude rubber. This decrement is considered to be decomposition by a microorganism.
2) It turned out that the molecular weight of crude rubber is decreasing clearly.
[0025]The biodegradable sample Kalter wax of seven to example 13 wax (vegetable system wax)
KARUNABA No. (vegetable system wax) 2
Camps Delia (vegetable system wax)
Soybean hydrogenated oil (vegetable system wax)
Paraffin wax (mineral system petroleum wax)
Montan wax (mineral system petroleum wax)
Rice wax (vegetable system wax)
Only the bacillus put in the polyethylene wax (comparative example 8) and the bacillus which consist of synthetic hydrocarbon, and was performed in the similar way without putting in a wax as the seven to comparative example 8 comparative example 7.
Parameter culture medium was prepared like the comparative example 1, added the powder of the above-mentioned wax 0.5g, and was performed. It was judged that biodegradable existence had biodegradability about some which measure the number of micro organisms of three months after and as which growth is regarded.
Result[0026]
[Table 4]

		生菌数(CFU)
実施例 7	カスターワックス	3.1×10^{4}
実施例 8	カルナバ2号	4.5×10^{5}
実施例 9	キャンデリア	1.5×10^{6}
実施例 10	大豆硬化油	4.8×10^{5}
実施例 11	パラフィンワックス	6.2×10^{5}
実施例 12	モンタンワックス	3.5×10^{5}
実施例 13	ライスワックス	1.7×10^{5}
比較例 7	菌のみ	1.9×10^{4}
比較例 8	ポリエチレンワックス	2.0×10^{4}

CFU:colony forming unit (生菌数)

[0027]It turns out that the number of microorganism in the culture medium of a vegetable system wax and mineral system petroleum wax is increased compared with the system which cannot enter a wax in waxes. Since the bacillus disassembled a vegetable system and mineral system petroleum wax and considered it as the nutrient, it increased.

[0028]The montan wax with comparative example 14 crude rubber (pale crepe, 10 times mastication), the China rosin, and biodegradability was heated, dissolution mixing was carried out, and hot melt adhesive was obtained. Evaluation of the shearing adhesive strength of the obtained hot melt adhesive and holding power was performed as follows, and Table 5 was obtained.

[0029]the adhesives obtained by the end of each aluminum plate (shearing adhesive strength 50 mm long, the side of 10 mm, and 0.5 mm in thickness) of one sheet -- heating and dissolving -- coating was carried out and the aluminum plate of the same size was pasted up. Then, shear strength was measured by a part for 5-mm/in hauling speed under 25 ** and the condition of 65% of relative humidity.

[0030]Holding power profitable **** hot melt adhesive 25 mm in width, and 50 mm in length. The stainless-steel board (SUS304) which built with the 0.1-mm aluminum plate in thickness, and ground 25 mm and a 25-mm-wide portion by sandpaper #280 was pasted, and the distance (mm) from which the aluminum plate shifted from the stainless-steel board, and fell by 1 kg of load was measured.

[0031]The soil burial burial place could be managed and set up the

level land near natural environment if possible. The burial place performed weeding out and removal of the pebble before burial. The soil before burial was taken out from the surface by about 10 cm, and it hung on the sieve, and was made as homogeneous as possible. The half of the uniformed soil could be returned and the surface was accustomed lightly. The sample (30 mm x 100 mm) (what was attached to the aluminum plate hot-melt-adhesive 0.5 mm in thickness) has been arranged on the surface of the earth. It returned with the residue of the uniformed soil, and surface of the earth was lightly accustomed so that a sample might be located in about 5 cm under surface of the earth. The place laid underground did not perform weeding out during a test period etc., but neglected them with the natural state. The sample after 180 days was dug up and the weight retention of the sample was investigated from the formula (1).

Result[0032]

[Table 5]

		実施例 14	実施例 15	実施例 16	実施例 17	実施例 18	比較例 9	比較例 10	比較例 11	比較例 12	比較例 13
天然ゴム	ペールクレープ 素練り10回	100	10	200	100	100		5	210	100	100
合成ゴム	SISブロックコポリマー						100				
粘着付与剤	生ロジン	100	100	100	100	100		100	100	100	100
	スチレンマレイン酸共重合体						100				
ワックス	モンタンワックス	50	50	50	10	200		50	50	5	210
	ポリエチレンワックス						50				
粘着特性	剥離接着力(kg/in)	1.0	0.5	0.8	0.5	0.5	1.0	<0.3	加熱しても溶解せず	固まり速度が遅い	<0.3
	保持力（分）	>60	>60	>60	15	>60	>60	12			50
生分解性	微生物の増殖（白濁の有無）	増（有）	増（有）	増（有）	増（有）	増（有）	無（無）	増（有）			増（有）
	土壌埋設(6カ月後)重量保持率	55%	60%	57%	58%	60%	100%	53%			58%

[0033]According to the Examples 14-18, adhesive strength was also good, and the result which has biodegradability was shown.

[0034]The shearing adhesive strength, holding power, and biodegradability of the hot melt adhesive which consists of composition ratio of the hot melt adhesive which consists of compounds, crude rubber other than the above and raw rosin, and a

wax as nine to comparative example 11 comparative example were shown in the comparative examples 9-11.

[0035]

[Effect of the Invention]The hot melt adhesive of this invention has biodegradability, and is excellent in the adhesion characteristic. The adhesives with which the processing is regarded as questionable are disassembled by the microorganism, and it is used as adhesives effective in the environmental problem in which a solvent volatilizes at the time of use and as for which things are not.

[Translation done.]